

Supporting Information

Promoting C–C bond coupling of benzyne and methyl ligands in electron deficient (triphos)Pt–CH₃⁺ complexes

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1. Experimental Details and Complex Characterization Data

1.1 General Methods

All reactions were performed under an inert atmosphere of dry N₂ with standard Schlenk techniques. All commercially available reagents were used as received without further purification. Acetonitrile was dried over calcium hydride, and dichloromethane and diethyl ether were passed through a column of alumina¹. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded on either a Bruker Avance 600 MHz or 400 MHz spectrometer at STP. NMR chemical shifts (δ) are reported in ppm and referenced to the residual solvent peaks (¹H, ¹³C{¹H}) or to an external standard (85% H₃PO₄ for ³¹P{¹H}). HRMS was performed by the Mass Spectrometry Laboratories of University of North Carolina at Chapel Hill. [(COD)Pt-o-tolyl(Cl)] was synthesized following a literature procedure,² as were [(triphos)PtMe][BF₄]³ and [Ph₂NH₂][BF₄].⁴

1.2 Preparation of Complexes

[(triphos)PtMe(C₆H₄)][BF₄], 2. To a flame-dried capped Schlenk flask under nitrogen atmosphere was added dry CsF (364.6 mg, 2.4 mmol) followed by anhydrous acetonitrile (10 mL). This slurry was subsequently stirred at 30°C for 2 h. To this solution was added 200 mg (0.24 mmol) of [(triphos)PtMe][BF₄] **1**, followed by 67 μ L of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.28 mmol); the reaction mixture was stirred for 18 h at rt. The resulting mixture was then passed through a 0.2 μ m PTFE syringe filter, the solvent removed under reduced pressure, the residue washed with diethyl ether (2 \times 3 mL), and the yellow solid dried under vacuum to yield 177.1 mg (90 %) of **2**. HRMS (EI) C₄₁H₄₀P₃Pt [M-BF₄]⁺/z calc. 820.1989 found 820.1982. ¹H NMR (600 MHz, CDCl₃): δ 0.72 (q, $J_{\text{Pt-H}} = 6.8$ Hz, $J_{\text{Pt-H}} = 55$ Hz, 3H, Me-Pt), 2.04 (m, 2H, CH₂-P), 2.97 (m, 2H, CH₂-P), 3.12 (m, 2H, CH₂-P), 3.25 (m, 2H, CH₂-P), 6.59 (m, 2H, C₆H₄), 6.99 (m, 2H, Ar), 7.03 (t, $J = 7.5$ Hz, 2H, Ar), 7.09 (m, 2H, C₆H₄), 7.13 (m, 8 H, Ar), 7.20 (t, $J = 7.6$ Hz, 1H, Ar), 7.27 (m, 2H, Ar, overlapping with residual CHCl₃), 7.52 (m, 6H, Ar), 7.90 (m, 4H, Ar). ³¹P{¹H} NMR: (242.9 MHz, CDCl₃): δ 20.3 (s, Pt satellites, $J_{\text{Pt-P}} = 2228$ Hz, 2P), 49.8 (s, Pt satellites, $J_{\text{Pt-P}} = 1185$ Hz, 1P). ¹³C{¹H} (150.9 MHz, CDCl₃): δ -9.7 (dt, $J_{\text{C-P}} = 98$ Hz, $J_{\text{C-P}} = 3.8$ Hz, Pt satellites $J_{\text{Pt-C}} = 389$ Hz, Me-Pt), 25.5, 30.1, 107.5 (m, Pt satellites, $J_{\text{Pt-C}} = 336$ Hz, C₆H₄), 117.7, 119.4, 119.8, 121.9, 125.6, 125.9, 128.4, 129.0, 130.5, 130.9, 131.1, 131.8, 133.3.

[(triphos)Pt(2-Me)Ph][BF₄], 3: This complex was prepared similarly to that reported for [(triphos)Pt-(2,4-Me₂)Ph][BF₄].⁵ To a solution of [(COD)Pt-o-tolyl(Cl)] (55.0 mg, 0.1 mmol) in dry dichloromethane (20 mL) was added triphos (53.5 mg, 0.1 mmol) under N₂ atmosphere. The solution was stirred for 30 min at room temperature and then an aqueous solution of NaBF₄ (108.9 mg, 1.0 mmol, in 5 mL H₂O) was added, and the resulting mixture was stirred for 15 min. After separation of the organic layer, extraction with dichloromethane (2 \times 5 mL) and removal of the solvent under reduced pressure, the final product was dried under vacuum to yield a pale yellow solid. Yield: 56 mg, 69 %; Note: The major species is assigned the *syn*-rotamer⁵ HRMS (ESI) for C₄₁H₄₀P₃Pt ([M-BF₄]⁺/z) calc. 820.1989, found 820.1988.

For the *syn*-rotamer, ¹H NMR (400 MHz, CDCl₃): δ 1.78 (s, 3H), 2.36-2.57 (m, 4H), 3.04-3.46 (m, 4H), 6.29 (m, with satellites, $J_{\text{PtH}} = 42.17$ Hz, 1H), 6.55 (m, 1H), 6.78 (d, 2H), 7.09 (m, 4H),

7.38-7.5 (m, 17H, Ar), 7.62 (m, 2H), 7.96 (m, 2H) ppm; ^{31}P NMR (161.9 MHz, CDCl_3): 35.7 (s, with Pt satellites, 2P, $^1\text{J}_{\text{PtP}} = 2760$ Hz) ppm, 91.7 (s, Pt satellites, 1P, $^1\text{J}_{\text{PtP}} = 1492$ Hz). For the *anti*-rotamer, ^1H NMR (400 MHz, CDCl_3): δ 0.40 (s, 3H), 2.13-2.30 (m, 4H), 2.79-2.94 (m, 4H), 6.45 (m, 1H), 6.72 (m, 1H), 6.86 (d, 2H), 7.19 (m, 4H), 7.38-7.8 (m, 21H, ArH); ^{31}P NMR (161.9 MHz, CDCl_3): 36.3 (s, Pt satellites, $J_{\text{PtP}} = 2706$ Hz) ppm, 91.7 (s, Pt satellites, $J_{\text{PtP}} = 1471$ Hz).

1.3 General Procedures for Protonolysis and Thermolysis Reactions

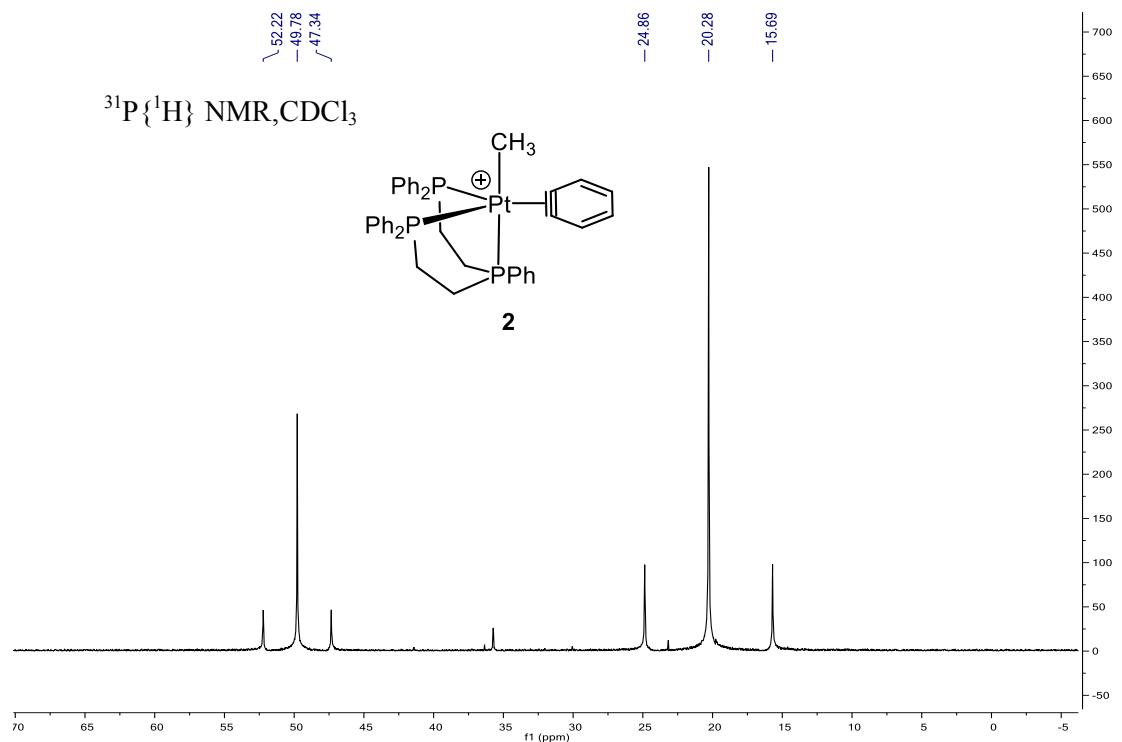
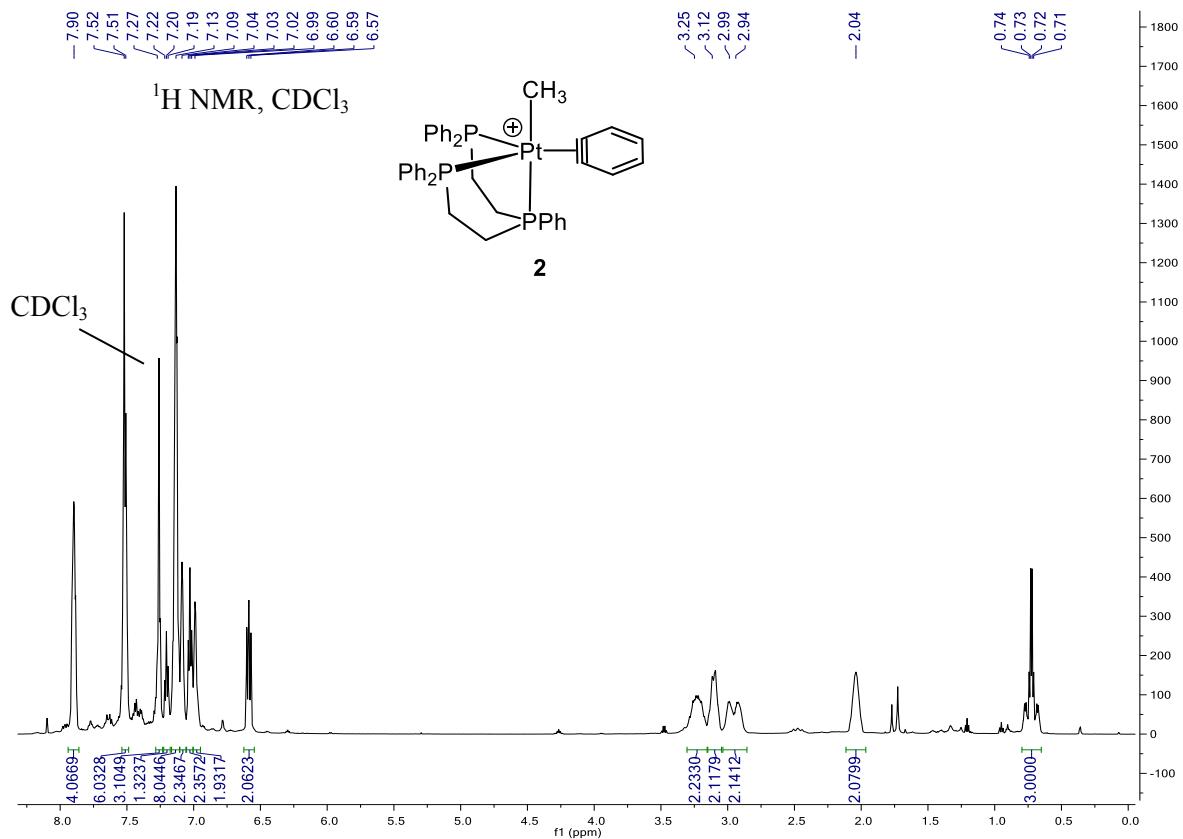
Reaction of [(triphos)PtMe(C_6H_4)][BF₄], 2, with [Ph₂NH₂][BF₄]: To a solution of [(triphos)PtMe(C_6H_4)][BF₄], 2, (10.0 mg, 0.012 mmol) in anhydrous CH₃CN (2 mL) was added [Ph₂NH₂][BF₄] (30.8 mg, 0.12 mmol, 10 eq) at room temperature. After stirring for 8 hours, complex 2, was converted to [(triphos)Pt(NCCH₃)]²⁺ and toluene.

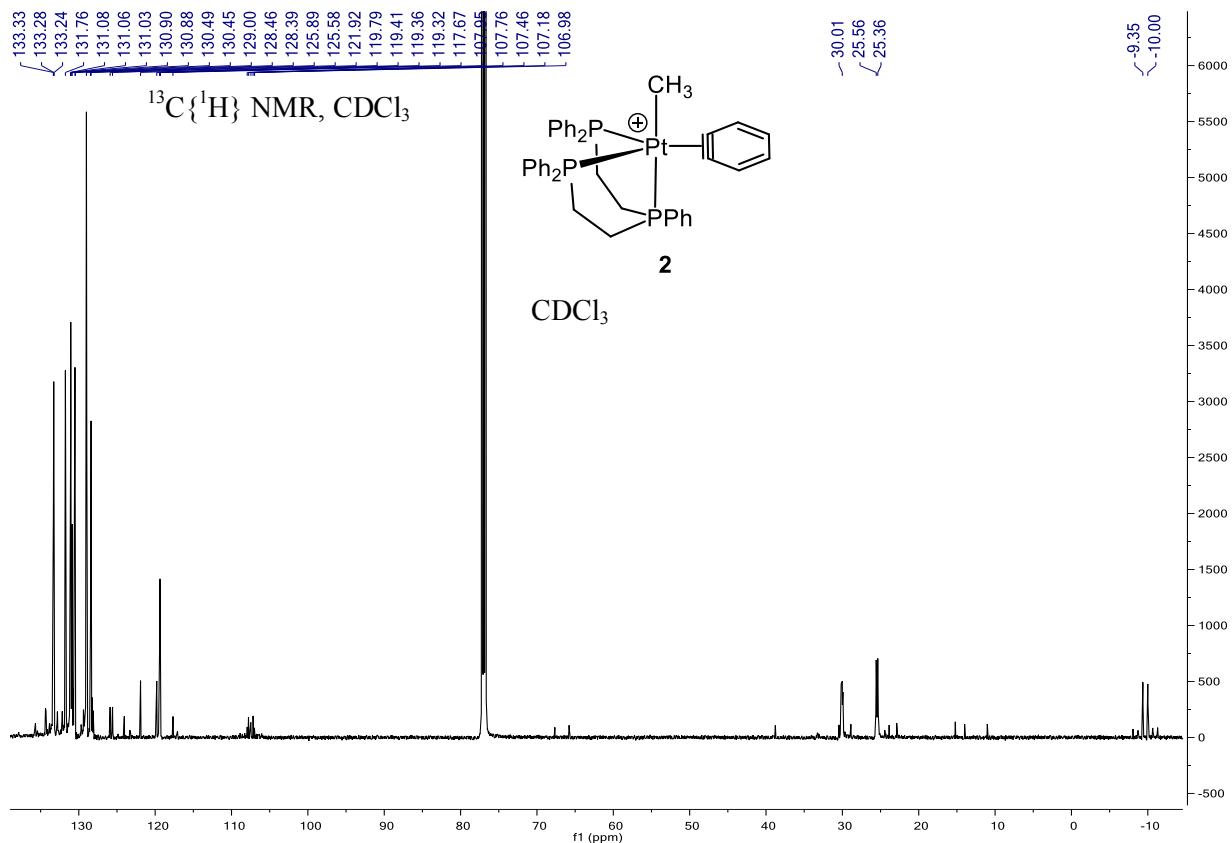
Reaction of [(triphos)Pt(2-Me)Ph][BF₄], 3, with [Ph₂NH₂][BF₄]: To a solution of [(triphos)Pt-(2-Me)Ph][BF₄], 3, (10.0 mg, 0.012 mmol) in anhydrous CH₃CN (2 mL) was added [Ph₂NH₂][BF₄] (30.8 mg, 0.12 mmol) at room temperature. After stirring for 2 days, 40% of complex 3 was converted to [(triphos)Pt(NCCH₃)]²⁺ and toluene.

Thermolysis of [(triphos)PtMe(C_6H_4)][BF₄], 2: In a sealed NMR tube, [(triphos)PtMe(C_6H_4)][BF₄], 2, (20 mg, 0.024 mmol) was dissolved in deuterated chlorobenzene (0.5 mL) and heated at 60 °C. Based on ^{31}P -NMR spectroscopy, complex 2, was converted to complex 1 and complex 3 in a 1: 2.4 ratio, respectively, after 3 days.

2. NMR Spectra of New Complexes

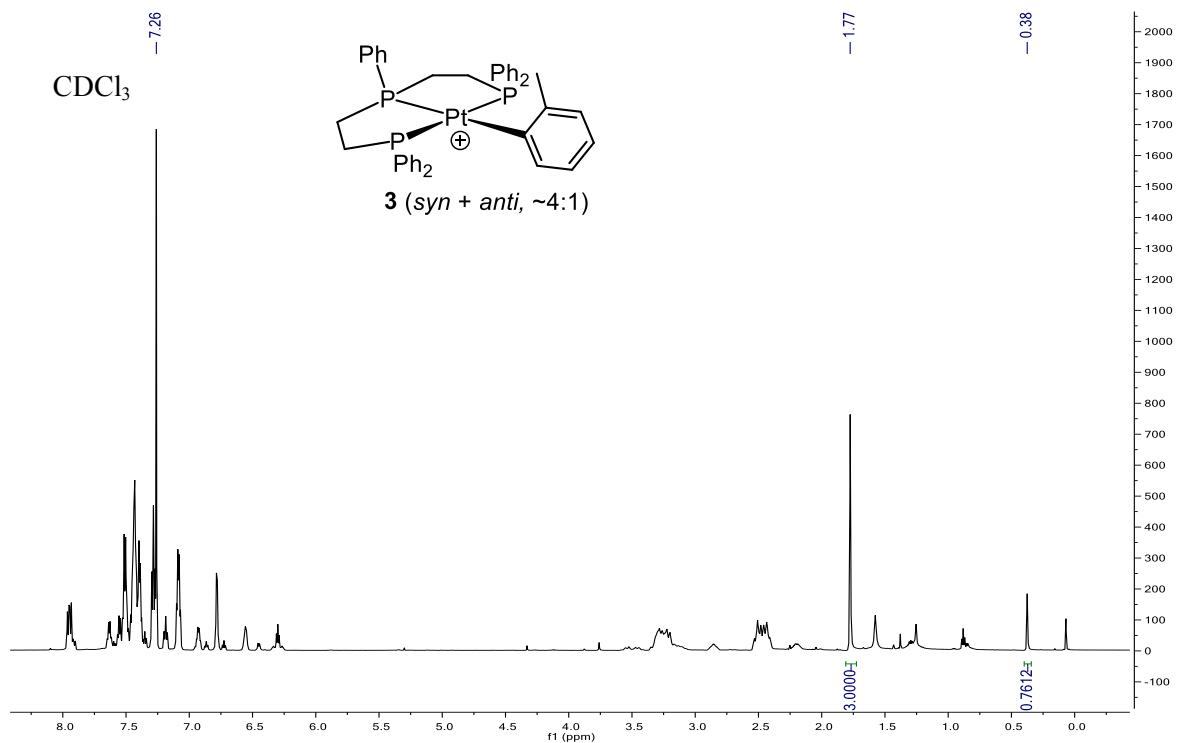
2.1 ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ of [(triphos)PtMe(C₆H₄)][BF₄], 2, in CDCl₃

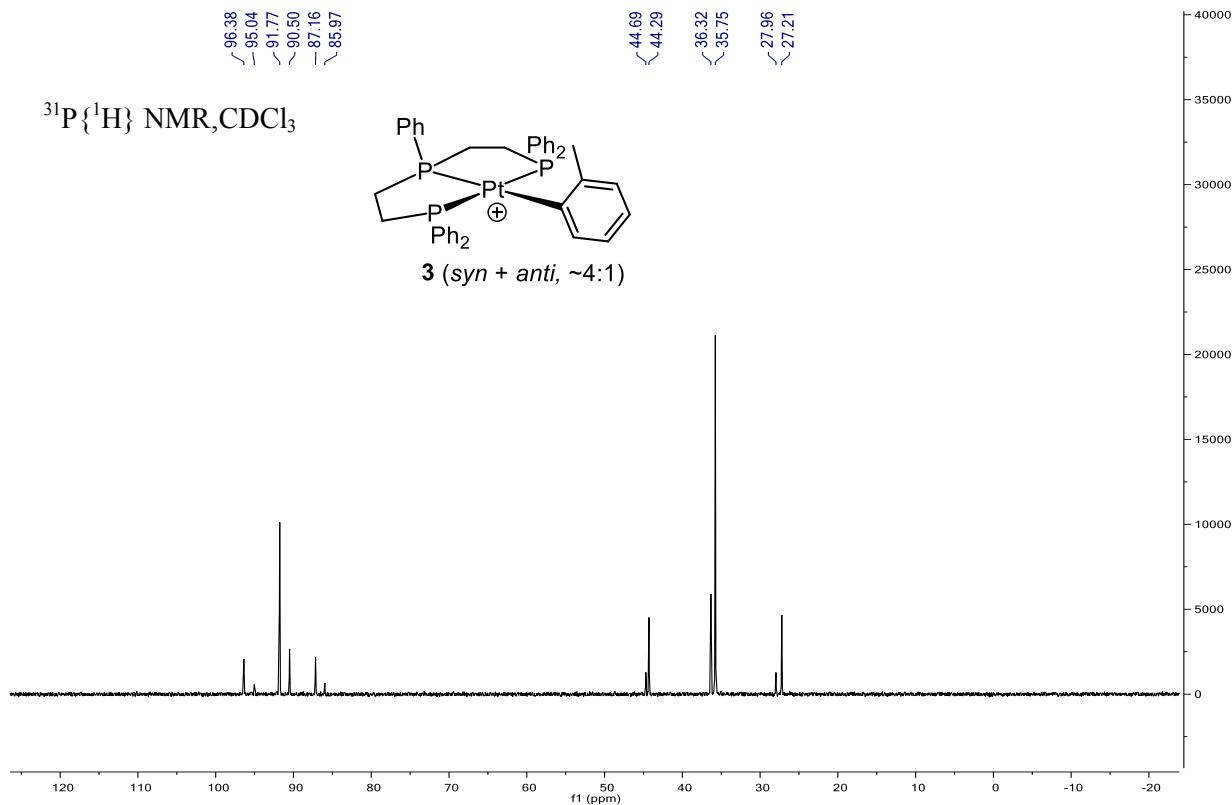




2.2 ¹H, ³¹P{¹H} and ¹³C{¹H} of [(triphos)Pt(2-Me)Ph][BF₄], 3, in CDCl₃

¹H NMR, CDCl₃





3. Computational Details

All calculations were carried out at the DFT/B3LYP^{6,7} level using the Gaussian 09 software package.⁸ The built-in 6-311G(d,p)⁹ basis set was used for all non-transition metal atoms, and the LANL2DZ (ECP)¹⁰⁻¹² basis set was used for Pt, with additional f-polarization (exp=0.993¹³). The ECP was obtained from the EMSL Basis Set Exchange.^{14,15} Complex geometries were fully optimized using standard gradient methods. Solution-phase calculations were performed by re-optimizing the structures with the polarized continuum method (IEFPCM¹⁶) with solvent parameters for acetonitrile. All free energy calculations were obtained by taking into account vibrational zero-point energies, thermal motions, and entropy contributions at standard conditions (298.15 K, 1 atm).

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